Defect studies and optical activation of Yb doped GaN

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Abstract. Wide band-gap semiconductors, particularly III-nitrides, became one of the most studied materials during the last decades. These compounds are the base of a new generation of optoelectronic devices operating in the UV-Blue region of the electromagnetic spectrum. Incorporation of rare-earth (RE) ions into nitrides creates new routes to build all-nitride electroluminescent devices, using the sharp intra-4f^n transitions of these elements. The introduction of the RE ions in the nitride lattice during the growth or by ion implantation creates defects which influence the optical behaviour of the doped region. In this work we report the results on Yb implanted GaN. A combination of techniques (Rutherford backscattering/Channeling and Photoluminescence) was used to assess the mechanisms responsible for the optical and structural behaviour of the doped materials. Lattice site location experiments showed that Yb is incorporated into positions slightly displaced from the Ga-site. Clearly the optical activity of the RE could be enhanced by orders of magnitude reducing the number of non-radiative recombination paths related with defects.

1. Introduction

The incorporation of lanthanide ions in GaN-based materials has generated much interest lately due to the development of blue, green and red emitting devices based on the intra-4f^n transitions of Tm^{3+}, Er^{3+} and Eu^{3+} ions [1-3]. Luminescence properties of GaN-based systems doped with rare earth (RE) ions have been widely studied on the basis of the crystal field splitting of the $^{2S+1}L_J$ manifolds of the 4f^n configurations. In nitride samples these ions mostly occupy the cation site symmetry (C_{3v}). Nevertheless they are often found in more than one distinct environment as observed using optical measurements. Extended X-ray absorption fine structure [4], emission channelling [5] and Rutherford backscattering spectrometry in the channelling geometry (RBS/C) [6,7] have shown that the majority of the RE ions occupy Ga-substitutional sites (C_{3v} symmetry) and some of the ions are slightly displaced from the Ga sites probably due to point defects in their vicinity.

In the visible spectral range other rare earth ions such as Tb^{3+}, Pr^{3+} and Sm^{3+} have also been studied by several research groups [8-12]. In the infrared Er^{3+} is known to be one of the most important ions as its $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition occurs at 1.54 µm which coincides with the minimum absorption wavelength region of silica based optical fibres. On the other hand Yb^{3+} (4f^{13}) despite the very simple scheme of levels with only the fundamental and excited multiplets ($^2F_{7/2}$ and $^2F_{5/2}$, respectively) which are separated by an energy of around 10000 cm^{-1} is one of the rare earth ions with scarce analysis in nitride hosts [13,14]. This RE ion besides the optical emissions can also be used as a sensitizer for other rare earth ions [15].

Here, we report on the optical activity of Yb^{3+} doped GaN layers produced using ion implantation and rapid thermal annealing treatments. After the implantation and each annealing step the samples were studied by RBS/C to asses the damage and lattice site location. Using above and below band gap photon energy excitation the intra-4f^{13} recombination between the multiplets $^2F_{5/2} \rightarrow {}^2F_{7/2}$ of the Yb^{3+} was observed.

2. Experimental Details

GaN layers were implanted with an energy of 150 keV and fluences of 5×10^{14} cm^{-2} and 5×10^{15} cm^{-2}. The as-implanted samples were further submitted to rapid thermal annealing (RTA) in flowing nitrogen during 120 s at 1000 °C using a proximity cap.

Ion beam analysis (RBS/C) was performed with 2.0 MeV He^+ ions and the backscattered particles were detected with solid state detectors placed at 140° and close to 180º with resolutions of 13 and 16 keV, respectively. A high precision (~0.01°) computer controlled goniometer was used to place the samples in position and perform the channelling measurements. The PL studies of the annealed samples were measured with above and below band gap excitation using as excitation sources the 325 nm laser line of a cw He-Cd laser, a 450 W Xe arc lamp coupled to a monochromator and the 488 nm laser line of a cw Ar^+ laser. The luminescence was dispersed using a Spex 1704 monochromator or a Fluorolog-3 Jobin Yvon-Spex. A Brucker 66V Fourier-transform spectrometer was also used for the infrared spectral region PL measurements. The signal was detected either by cooled Hamamatsu photomultipliers (R928, H9170-75) or by a North-Coast EO-817 liquid nitrogen cooled germanium detector.

3. Results and discussion

The aligned RBS/C spectra of the ytterbium as implanted GaN clearly show the damage produced by the implanted ions, Fig.1.

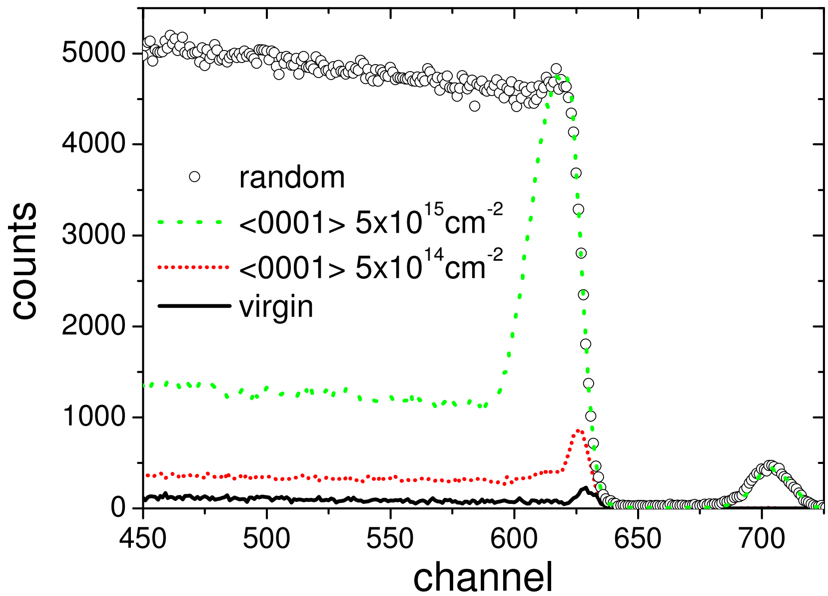

Figure 1. Random and <0001>-axis aligned RBS spectra obtained with 2.0 MeV He^+ before (virgin) and after implantation with 150 keV Yb ions to a fluence of 5×10^{14} and 5×0^{15} at/cm^2, at room temperature.

The backscattering yield of the aligned spectrum for the sample implanted with the highest fluence overlaps in the implanted region with the random spectrum revealing the complete loss of long range order typical for high fluence implantation [16,17]. For the lower fluence, besides the surface peak a second peak is visible close the end of range of the implanted ions in agreement with the behaviour observed for other RE in GaN [6, 18]. The low damage level in the implanted region in this sample allows the lattice site location of the Yb ions in the GaN structure. Detailed angular scans along the <0001> and <10-11> axial directions are shown in Figure 2. The close agreement between the Ga and Yb curves demonstrates the incorporation of the Yb ions in Ga sites. The Yb scan is found slightly narrower than the one for Ga indicating a small displacement from the perfect substitutional site. Similar results were reported for measurements using the emission channelling technique [14].

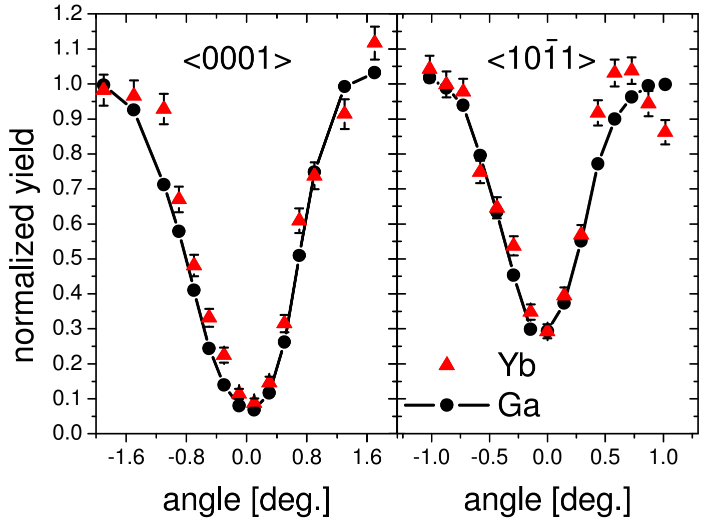

Figure 2. Yb- and Ga-Angular scans for the <0001> and <10-11> axes obtained directly after the implantation with 5×10^{14} at/cm^{-2}..

After annealing we observe a small decrease of the implantation damage and the angular scan along the <0001> axis seems to indicate an increase of the displacement of the Yb ions perpendicular to the c-axis, Fig.3. This displacement is responsible for the narrowing of the Yb curve with respect to the GaN one. Emission channelling [14] did not show an increased displacement after annealing. This difference could be attributed to the much higher ion fluence used in the present study and suggests that implantation defects are responsible for the displacement of Yb. The sample implanted on the higher fluence showed a complete decomposition of the samples' surface after annealing. The highly damaged surface layer sublimates and Yb segregates at the surface upon high temperature annealing.

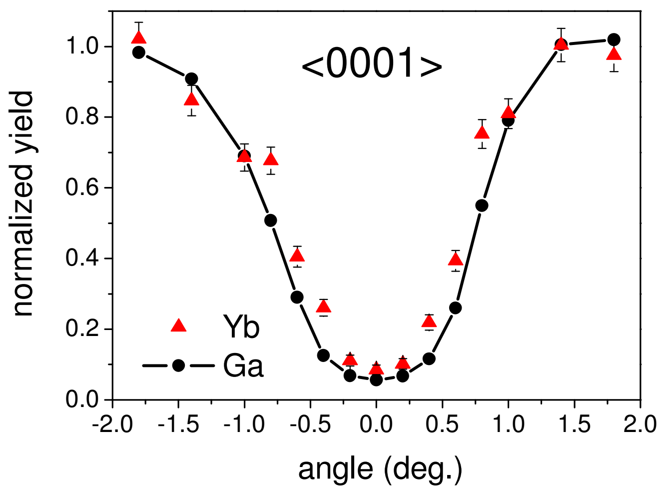

Figure 3. Angular scans obtained for the sample implanted with $5x10^{14}$ cm^{-2} after annealing for the <0001> axes.

Despite the relatively low damage level and the high fraction of Yb in regular sites in the low-fluence sample no PL signal was observed directly after the implantation. Figure 4 shows the low temperature PL spectra of annealed GaN:Yb samples obtained with above band gap excitation. The spectrum shows the typical D^0X feature of GaN layers at ~357 nm followed by broad emission bands. As observed the dominant optical active defect is different in both samples being the sample implanted with $5x10^{15}$ cm^{-2} dominated by a violet recombination with maxima at 382 nm and 414 nm.

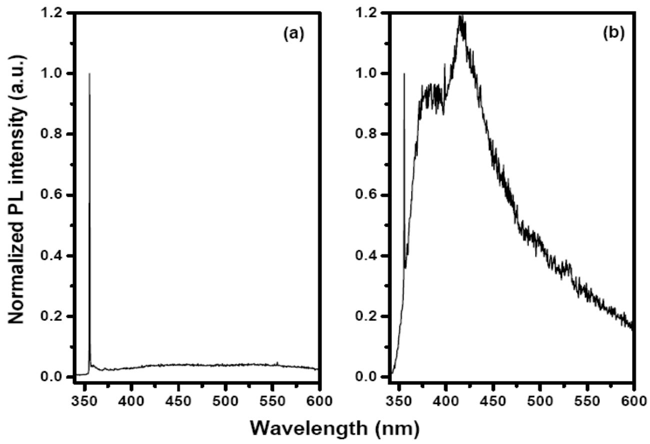

Figure 4. 12 K PL spectra of samples implanted with $5x10^{14}$ cm^{-2} (a) and $5x10^{15}$ cm^{-2} (b).

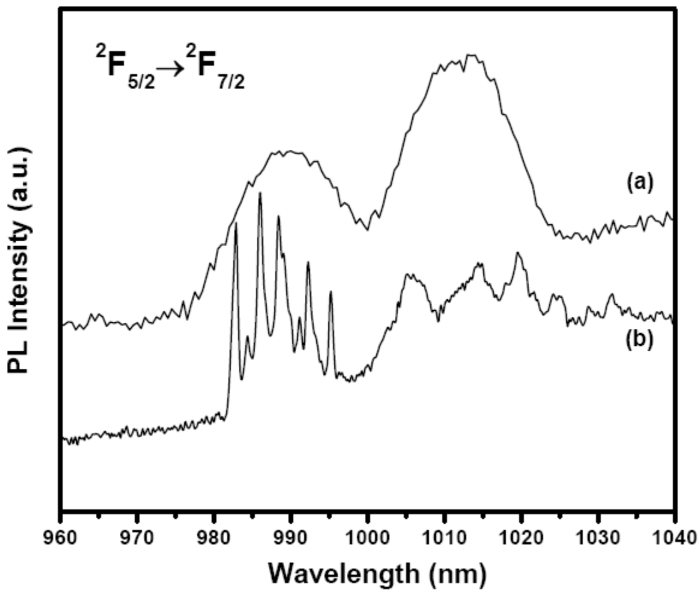

Figure 5. (a) 12 K low resolution PL spectra obtained with 357 nm photons using a Xe lamp coupled to a monochromator and (b) 70 K high resolved spectra obtained with a 488 nm excitation line of an Ar^+ laser using a FTIR system.

Figure 5 shows the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb^{3+} ion observed in our doped and annealed low-fluence sample. The spectra were taken under different excitation conditions and at different temperatures. They were also measured in different set-ups with different resolution conditions.

One of the main characteristics corresponds to the excitation paths for the observed emission. PLE monitored at the intraionic emission maxima shown in Figure 6 indicates that besides the above band gap excitation the intraionic Yb^{3+} luminescence is excited via band gap electronic levels that match both the donor bound exciton recombination and the violet band. Furthermore, and in accordance with the data shown in Figure 5, the intraionic emission can also be excited by photons with lower energy such that ones corresponding to the 488 nm wavelength.

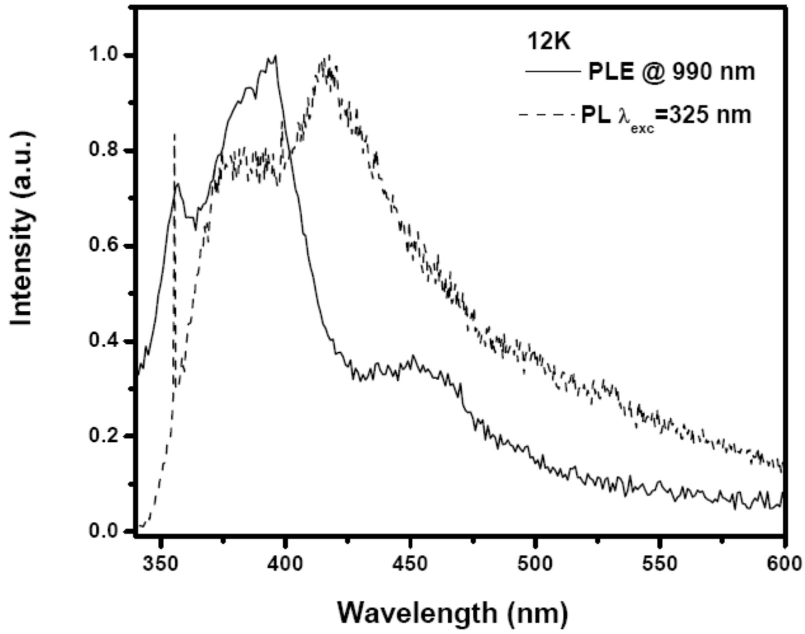

Figure 6. 12 K PL spectra (dash line) and PLE spectra (full line) monitored at 990 nm.

RBS/C measurements clearly evidence that the Yb^{3+} occupies near-substitutional Ga sites. In C_{3v} site symmetry the manifolds $^2F_{7/2}$ and $^2F_{5/2}$ split into four and three Kramers doublets, respectively. At lower temperatures and assuming that only the lowest energy level of the excited $^2F_{5/2}$ multiplet is populated four transitions are expected for the intraionic recombination. However, in accordance with previous observations [13] the observed spectra (Fig. 5) are rather complex which cannot be accounted for this simple explanation. Thermally populated stark levels, vibronic coupling effects and/or multiple optically active centres cannot be excluded. The slight displacement from the perfect substitutional site evidenced by RBS/C may point to the interaction of Yb with defects which could be the origin of multiple optically active centres. Furthermore, a detailed analysis of the influence of the different excitation mechanisms on the resolved PL must be realized.

4. Conclusions

Implantation of GaN with Yb leads to the incorporation of Yb into Ga-sites. After annealing a clear displacement of the Yb from the regular lattice site ions is observed occurring at the same time as the partial damage recovery of the GaN crystal indicating an interaction of Yb ions with defects. The optical activity of the samples after implantation was totally quenched. The annealed GaN:Yb samples studied using low temperature PL and PLE spectra reveal that optical activation of Yb is achieved. The infrared emission characterized by multiple narrow features which cannot be explained by a simple model assuming that the emission is provided by the lowest energy level from the excited multiplet. The analysed data also indicate that the intraionic recombination can be excited using above or below band gap excitation being some of the energy levels coincident with the donor bound exciton recombination and violet emission.

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